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On the Transition State of the Thermal Propene Elimination from Allylphosphines

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ABSTRACT

Diallyltetramethylpiperidinophosphine **1**, *diallyldiisopropylaminophosphine* **2**, *and diallylmesitylphosphine* **3** *were pyrolyzed in a stirred flow reactor over the temperature range 400–450°C, using toluene as carrier gas, producing, in all cases, mixtures of phosphorus-containing products. The pyrolysis of* **1** *produced 1-tetramethylpiperidino-1-phosphabutadiene, in addition to a mixture of phosphines and polyphosphines. Compound* **2** *produced the azadiphosphole* **4**, *the phosphinine* **5**, *allylphosphine, and diisopropylaminophosphine as major phosphorated products. The pyrolysis of* **3** *produced a mixture of phosphines and polyphosphines. The complex mixture generated by the three diallylphosphines indicates the formation of free radicals during their pyrolyses. AM1 calculations on the transition state of an expected retroene-type propene elimination reaction showed that, due to the phosphaalkene character of the transition state, the structure of the latter is very rigid and sensitive to steric effects. Steric hindrance of the substituents on the phosphorus atom compels the molecule to distort the half-chair transition structure, causing a rise on the activation energy to values in the range of a homolytic P–C bond dissociation energy.*

INTRODUCTION

In previous work [1], we reported the generation of some transient 1-phospha-1,3-butadienes unsubstituted on the carbon chain, by pyrolysis of the corresponding diallyl phosphines (Figure 1).

The generated phosphabutadienes have shown a certain stability at low temperature, enough to characterize them by ^{31}P-NMR spectroscopy. A subsequent kinetic study [2] permitted the postulation of a unimolecular reaction mechanism through a six-center cyclic transition state (Figure 2), also valid for other allyl phosphines having a hydrogen atom in the α position with respect to the phosphorus atom [2].

The potential utilization of the phosphabutadienes generated by this novel reaction as synthetic intermediates in preparative heterocyclic chemistry (see, for example, Ref. [3]) makes it interesting to try to prepare a family of stable phosphabutadienes, starting from the easily available diallylphosphines with diverse substituents on the phosphorus atom.

Having in mind that one of the common methods for stabilizing phosphaalkenes is to protect the phosphorus–carbon double bond by bulky substituents on the phosphorus atom [4], we report here our results on the thermal decomposition of diallylphosphines having sterically hindered substituents, such as tetramethylpiperidino (TMP), diisopropylamino and mesityl (2, 4, 6-$(CH_3)_3C_6H_2$), on the phosphorus

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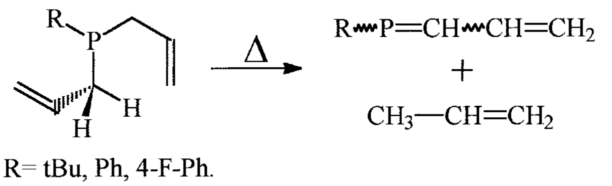


FIGURE 1

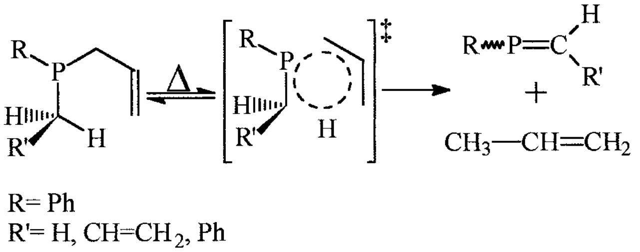


FIGURE 2

atom. Additionally, we discuss a theoretical study, using the semiempirical AM1 method [5], of the transition state of the retroene elimination of propene from allylphosphines in order to explain the unexpected observed reactivity.

RESULTS AND DISCUSSION

The pyrolysis of diallyltetramethylpiperidinophosphine **1** over the temperature range 400–450°C, using toluene as carrier gas, produces a complex mixture that, collected in a liquid-nitrogen trap, presents an intense yellow color that disappears at room temperature. A gas chromatography analysis of the gases produced showed a composition of about 2% C_2, 78% propene, 19% C_4, and traces of other heavier hydrocarbon products. The ^{31}P-NMR analysis of the mixture (Table 1) at -50°C showed the formation of the expected 1-phosphabutadiene ($\delta = 195$) in 10–15% yield; nevertheless, the spectra showed predominantly signals whose chemical shift can be attributed to phosphines and polyphosphines as the main products. No remarkable changes are observed when the spectra are recorded at room temperature.

Under the same conditions, diallyl(diisopropylamino)phosphine **2** showed the formation of about 88% of propene, 7% of propane, and other heavier products, such as gases. From the analysis of the ^{31}P-NMR spectra, one can observe the formation, in 15–20% yield, of a product that seems to be the 1-isopropyl-5-methyl-1,2,3-azadiphosphole **4** on the basis of the spectroscopic data (Table 1). This compound has been reported [6,7] as showing a ^{31}P chemical shift of $\delta = 323$ and $\delta = 244$ with a $^1J_{PP} =$ 480 Hz; we think that the observed small differences in the chemical shift may be due to mixture effects, since the pure product has not been isolated. However, the value of the coupling constant and the fragmentation pattern in the mass spectra are both very similar to the reported ones [7]. Besides the azadiphosphole, we observed formation of small amounts of the diphosphinine **5** (10%) (Table 1), arising from a [4+2] cycloaddition reaction of the expected 1-phosphabutadiene [1,2,8], together with allylphosphine (10–15%), diisopropylaminophosphine (10%), and other products, probably polyphosphines, all products being assigned on the basis of their ^{31}P chemical shift values and their gas chromatography–mass spectroscopy (GC-MS) analysis.

Pyrolysis of diallylmesitylphosphine **3** under similar conditions yielded a more complex mixture of products. The analysis of the gases showed a composition of about 3% C_2, 87% propene, 4.5% C_4, and other nonidentified heavier products. The ^{31}P-NMR analysis of the nonvolatiles showed the formation of a mixture of phosphines and polyphosphines, among which one can distinguish mesitylphosphine (Table 1).

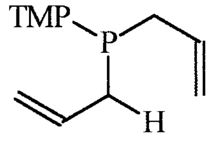
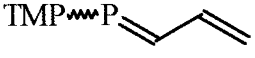
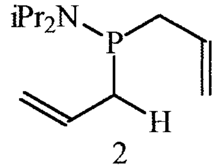
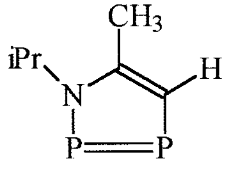
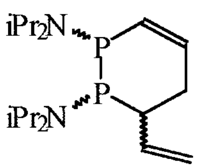
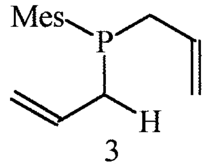
No further analysis of the reaction products was performed, since, in these three cases, the reaction did not follow the expected retroene fragmentation, producing instead complex mixtures of phosphorus derivatives. It seemed evident that the observed fragmentation pattern can best be explained by the formation of free radicals during the reaction.

Nevertheless, with the aim to understand better this unexpected reactivity, and to verify that the presence of bulky substituents prevents the molecule from achieving the appropriate transition-state geometry of a retroene reaction, we have performed theoretical studies of the transition states of retroene reactions using the semiempirical AM1 method [5]. Calculations were performed on four allylphosphines (Figure 3).

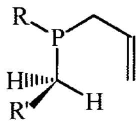
Phosphines **6**, **7**, and **8**, which are known decompose thermally by the retroene pathway [2], were chosen in order to verify that this method can be used for this qualitative analysis. We then computed the transition state on diallylmesitylphosphine **3**, which apparently prefers a homolytic dissociation pathway, in order to see what is different. The computed transition structures were confirmed by the presence of only one negative eigenvalue in the hessian matrix.

In Table 2 are reported the computed activation energies for the chosen allylphosphines and the experimentally observed *Ea* values for propene elimination. The calculations overestimate the activation

TABLE 1 Spectroscopic Data of Products Detected in the Pyrolyses of Diallylphosphines 1–3

Reactant	Product	Products spectroscopic data (^{31}P NMR (CDCl$_3$) and GC-MS)
 1		$\delta = 195$; m/e (%) = 211 (100%) M$^+$
	Phosphines and Polyphosphines	$-75 < \delta > -107$ $180\ \mathrm{Hz} < J_{PH} > 210\ \mathrm{Hz}$
 2	 4	$\delta = 318.4$; $\delta = 261.4$; $^1J_{PP} = 477$ Hz $^2J_{PH} = 41.8$ Hz m/e (%) = 159 (40%) M$^+$, 117 (100%) M$^+$-C$_3$H$_6$, 84 (80%) iPrNCCH$_3^+$, 75 (15%) PPCH$^+$,
	 5	$\delta = 48.3$; $\delta = -50.5$; $^1J_{PP} = 250.6$ Hz m/e (%) = 342 (20%) M$^+$, 315 (15%) M$^+$-C$_2$H$_3$, 262 (35%) (iPr$_2$NP)$_2^+$
	CH_2=CH-CH_2PH_2	$\delta = -134$, $^1J_{PH} = 191$ Hz
	iPr$_2$NPH$_2$	$\delta = -82$, $^1J_{PH} = 194$ Hz
 3	Mes−PH$_2$	$\delta = 156.6$, $^1J_{PH} = 205$ Hz
	Phosphines and Polyphosphines	$-70 < \delta > -108$ $190\ \mathrm{Hz} < J_{PH} > 218\ \mathrm{Hz}$

TMP = 2,2,6,6-tetramethylpiperidino.
Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$.



6 : R= Ph, R'= H
7 : R= Ph, R'= CH=CH$_2$
8 : R= Ph, R'= CH$_2$Ph
3 : R= Mesityl, R'= CH=CH$_2$

FIGURE 3

energies by a factor of about 2.51. Using this as scaling factor, one can consider that the corrected activation energies obtained by these calculations reproduce the experimental values showing an overestimation of about 10% in the case of allylbenzylphenylphosphine 8, acceptable for the method and for our qualitative analysis. On consideration of the activation energy for the putative propene elimination from diallylmesitylphosphine 3, it can be seen that the computed value is too large (240 kJ mol^{-1}), compared with values for molecules that are known to follow a retroene mechanism for propene elimination. The figure 240 kJ mol^{-1}, however, is in the range of values for homolytic dissociation of some alkyl phosphines [9], explaining why radical splitting in this case competes favorably with the retroene mechanism.

Selected bond lengths and bond angles of the computed transition structures, for the atoms directly involved in the transition state, as represented in Figure 4a, are listed in Tables 3 and 4. No remarkable geometrical differences are observed among the different phosphines. The results show analogies with reported values for bond lengths and bond angles obtained by ab initio calculations for the

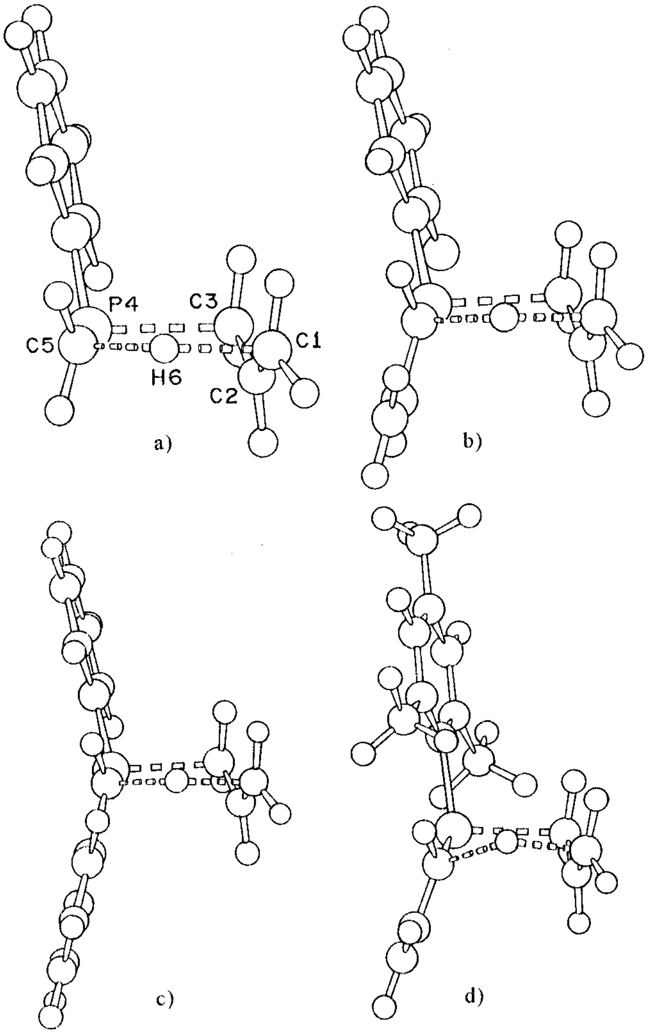


FIGURE 4 AM1 transition structure of the retroene propene elimination from allylphosphines: (a) allylmethylphenylphosphine **6**; (b) diallylphenylphosphine **7**; (c) allylbenzylphenylphosphine **8**; (d) diallylmesitylphosphine **3**.

TABLE 2 Activation Energies for Propene Elimination in kJ/mol

Phosphine	*Ea*	*Ea(corr)*[a]	*Ea(exp)*[b]
6	354	141	144 ± 9
7	365.2	146	143 ± 4
8	388.6	155	135 ± 6
3	602	240	—

[a] Corrected activation energy: *Ea*(corr) = *Ea*/2.51.
[b] Experimental activation energy.

TABLE 3 Selected Bond Lengths in the Computed Transition State (Å)[a]

Phosphine	*C1–C2*	*C2–C3*	*C3–P4*	*P4–C5*	*C5–H6*	*H6–C1*
6	1.41	1.40	2.30	1.66	1.67	1.74
7	1.41	1.42	2.30	1.64	1.78	1.67
8	1.40	1.40	2.29	1.65	1.73	1.68
3	1.41	1.41	2.34	1.69	1.89	1.69

[a] Atom numbers as in Figure 4.

ene reactions of ethylene with formaldehyde and propene [10,11], and with values obtained by semiempirical calculations for different retroene-type reactions [12–15].

The C–C bond lengths for the propene moiety about to be eliminated during the reaction show almost the same value, 1.41 Å, intermediate between a single and a double bond, pointing out the displacement of the double bond in the propene moiety during the reaction. The C3–P4 and C5–H6 bonds to be broken are remarkably stretched, 2.30 and about 1.70 Å, respectively, instead of the characteristic corresponding values of 1.85 Å [9] and 1.10 Å. At the same time, the P4–C5 bond, a bond to become double, presents an average value of 1.65 Å, in the normal range for a P–C double bond [4], showing that the transition state is considerably productlike. The hydrogen atom to be transferred from C5 to C1 is located slightly closer to the C1 atom and almost equidistant to the two other hydrogen atoms on the C1 carbon atom, improving the orbital overlap between H6 and C1. The P4 and C3 atoms are situated so as to maintain optimum orbital overlap in the transition state. Both P4 and C3 atoms, which change hybridization from *sp*3 to *sp*2, show a geometry between these two states. A remarkable difference, however, is observed between the C1H6C5 angle of the migrating hydrogen, around 133° in our calculations, and the reported 156° for the ene reaction [10–14].

For compounds **6**, **7**, and **8**, the transition structure resembles somewhat a half chair (Figures 4a–4c), where C1, C2, and C3 are located in a plane, and the H atoms on the C1 and C3 carbon atoms are slightly out of the plane, showing a geometry intermediate between the characteristic sp^2 and sp^3 hybridization geometries for these two carbon atoms. C3, P4, C5, H6, and C1 are located in nearly the same plane (Figures 4a–4c).

The computed transition structure for molecule **3** (Figure 4d) is more boat-shaped than the others (Figures 4a–4c). One can think that the large phosphaalkene character of the P4–C5 bond in the transition state makes the structure of the transition state very rigid and sensitive to steric effects. In **3**,

TABLE 4 Selected Bond Angles in the Transition State (deg)[a]

Phosphine	*C1C2C3*	*C2C3P4*	*C3P4C5*	*P4C5H6*	*C5H6C1*	*H6C1C2*
6	125.0	102.5	99.1	118.8	134.5	90.8
7	124.0	102.9	99.1	118.0	133.3	92.8
8	124.7	102.4	99.0	118.7	132.9	92.8
3	124.6	101.0	99.9	107.6	127.7	93.0

[a] Atom numbers as in Figure 4.

for example, the steric hindrance of the substituent on the phosphorus atom compels the molecule to distort the half-chair transition structure, raising the activation energy. The rigidity of the transition structure could also explain the experimental values of the activation entropy for propene elimination from allylphosphines [2], corresponding to frequency factors in the lower limit of accepted values for six-membered cyclic transition states.

In conclusion, the thermal decomposition of sterically hindered diallylphosphines produced complex mixtures of products, indicating the generation of free radicals during their pyrolyses. The AM1 calculations of the transition state of the propene elimination from allylphosphines, made in order to evaluate these results, showed that the transition structure is considerably productlike and very rigid. Bulky substituents on the phosphorus atom compel the molecule to distort the half-chair transition structure, causing the activation energy to rise to values in the range of homolytic P–C bond dissociation energies.

EXPERIMENTAL

^{1}H, ^{13}G, and ^{31}P-NMR spectra were recorded on a Bruker AM-300 instrument. Mass spectra were obtained on a Kratos GLCMS RFA25 instrument. Published methods where used for the synthesis of dichloro(tetramethylpiperidino)phosphine [16] and dichloromesitylphosphine [17].

Synthesis of Diallylphosphines 1, 2, *and* 3

In a typical procedure, a filtered solution of 0.242 mol of allylmagnesium bromide [18] was added dropwise to a stirred solution of 0.11 mol of the corresponding dichlorophosphine in 100 mL of freshly distilled ether cooled at −78°C. When the addition had been finished, the mixture was stirred at room temperature for 2 hours, filtered, and the solvent evaporated. The diallylphosphine was distilled under reduced pressure through a 15 cm vigreux column (70–85% yield).

Diallyltetramethylpiperidinophosphine 1: Liquid bp: 92–95°C/0.1 torr. ^{31}P NMR ($CDCl_3$, H_3PO_4 ext): $\delta = 34.7$; ^{13}C NMR ($CDCl_3$, Tms ext): $\delta = 17.7$ (s, CH_2), $\delta = 31.6$ (s, CH_2), $\delta = 33.7$ (d, $^{3}J_{PC} = 22.1$ Hz, CH_3), $\delta = 38.9$ (d, $^{1}J_{PC} = 25.1$ Hz, CH_2 allyl), $\delta = 56.6$ (d, $^{2}J_{PC} = 30.9$ Hz, $\underline{C}(CH_3)_2$), $\delta = 115.8$ (d, $^{2}J_{PC} = 11.6$ Hz, $CH{=}\underline{C}H_2$), $\delta = 136.2$ (d, $^{3}J_{PC} = 17.7$ Hz, $\underline{C}H{=}CH_2$); ^{1}H NMR ($CDCl_3$, Tms ext): $\delta = 1.37$ (m, 18H, TMP), $\delta = 2.69$ (m, 4H, CH_2), $\delta = 5.10$ (m, 4H, $CH{=}C\underline{H}_2$), $\delta = 6.02$ (m, 2H, $C\underline{H}{=}CH_2$).

Diallyldiisopropylaminophosphine 2: Liquid bp: 83–87°C/0.1 torr. ^{31}P NMR ($CDCl_3$, H_3PO_4 ext): $\delta = 26.9$; ^{13}C NMR ($CDCl_3$, Tms ext): $\delta = 23.8$ (d, $^{3}J_{PC} = 5.7$ Hz, CH_3), $\delta = 34.8$ (d, $^{1}J_{PC} = 17$ Hz, CH_2), $\delta = 45$ (d, $^{2}J_{PC} = 7.4$ Hz, $\underline{C}H(CH_3)_2$), $\delta = 115.7$ (d, $^{3}J_{PC} = 10$ Hz, $CH{=}\underline{C}H_2$), $\delta = 134.6$ (d, $^{2}J_{PC} = 11.8$ Hz, $\underline{C}H{=}CH_2$); ^{1}H NMR ($CDCl_3$, Tms ext): $\delta = 1.03$ (d, $^{3}J_{PC} = 6.7$ Hz, 12H, CH_3), $\delta = 2.27$ (m, 4H, CH_2), $\delta = 3.25$ (m, 2H, CH), $\delta = 4.95$ (m, 4H, $CH{=}C\underline{H}_2$), $\delta = 5.77$ (m, 2H, $C\underline{H}{=}CH_2$).

Diallylmesitylphosphine 3: Liquid bp: 112–114°C/0.1 torr. ^{31}P NMR ($CDCl_3$, H_3PO_4 ext): $\delta = -33.2$; ^{13}C NMR ($CDCl_3$, Tms ext): $\delta = 20.8$ (s, *p*-CH_3), $\delta = 23.4$ (d, $^{3}J_{PC} = 18.3$ Hz, *o*-CH_3), $\delta = 31.3$ (d, $^{1}J_{PC} = 16.4$ Hz, CH_2), $\delta = 116$ (d, $^{3}J_{PC} = 10.9$ Hz, $CH{=}\underline{C}H_2$),), $\delta = 128.9$ (d, $^{2}J_{PC} = 16.5$ Hz, *m*-C); $\delta = 129.6$ (d, $^{3}J_{PC} = 3.5$ Hz, *o*-C), $\delta = 134.5$ (d, $^{2}J_{PC} = 12.1$ Hz, $\underline{C}H{=}CH_2$), $\delta = 138.9$ (s, *p*-C), $\delta = 144.4$ (d, $^{1}J_{PC} = 14.6$ Hz, *i*-C); ^{1}H NMR ($CDCl_3$, Tms ext): $\delta = 2.27$ (s, 3H, *p*-CH_3), $\delta = 2.56$ (s, 6H, *o*-CH_3), $\delta = 2.78$ (d, $^{1}J_{PH} = 7.6$ Hz, 4H, CH_2),), $\delta = 5.04$ (m, 4H, $CH{=}C\underline{H}_2$), $\delta = 5.80$ (m, 2H, $C\underline{H}{=}CH_2$), 6.86 (s, 2H, *m*-H).

The phosphines were pyrolyzed in a 265 mL stirred flow reactor [19] over the temperature range of 400–450°C and total pressures between 7 and 21 torr, using toluene as carrier gas. The outflow from the reactor was trapped at −190°C. It was then fractionated. The gases were collected at −190°C and analyzed by gas chromatography in a 4 m × 3.2 mm O.D., 80/100 mesh activated Al_2O_3 column at 170°C using a flame ionization detector.

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